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New perspectives on forbidden symmetries, quasicrystals, and Penrose tilings

(crystallography/quasiperiodicity/icosahedral alloys)

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ABSTRACT Quasicrystals are solids with quasiperiodic atomic structures and symmetries forbidden to ordinary periodic crystals—e.g., 5-fold symmetry axes. A powerful model for understanding their structure and properties has been the two-dimensional Penrose tiling. Recently discovered properties of Penrose tilings suggest a simple picture of the structure of quasicrystals and shed new light on why they form. The results show that quasicrystals can be constructed from a single repeating cluster of atoms and that the rigid matching rules of Penrose tilings can be replaced by more physically plausible cluster energetics. The new concepts make the conditions for forming quasicrystals appear to be closely related to the conditions for forming periodic crystals.

About a dozen years ago, a new class of solids was discovered that exhibits symmetries (e.g., 5-fold symmetry axes) that were thought to be strictly forbidden. The new materials, dubbed quasicrystals, challenge conventional ideas about symmetry and order in solids. Ever since their discovery, the key puzzle has been: Why do atoms form a complex quasicrystal pattern rather than a regularly repeating crystal arrangement? A leading proposal has been that atoms arrange into two or more clusters analogous to tiles in a Penrose tiling (1) and have interactions that mimic matching rules (2–4). This model has been criticized, though, because the rules seem too complicated to be manifested in the simple atomic interactions of metal alloys. This paper focuses on recent discoveries about Penrose tilings that suggest that the conditions for making quasicrystals are much less complicated than had been thought (4); in fact, they are very similar to conditions for forming ordinary crystals.

The newly discovered properties of Penrose tilings address the two principal concerns with the Penrose tiling model of quasicrystals. One result is that a quasiperiodic tiling can be forced using only a single type of tile, instead of the two different types invoked in a Penrose tiling. The second result is that matching rules can be discarded in favor of maximizing the density of a chosen cluster of tiles. If one imagines the tile cluster to represent some energetically preferred atomic cluster, then minimizing free energy would naturally maximize the cluster density. These ideas had been conjectured previously (5) but have now been established rigorously by my collaborator Hyeon-Chai Jeong and myself, inspired by results from German mathematician Petra Gummelt (6, 7). From these results, there arises a natural explanation of why quasicrystals form and a new appreciation for the subtleties of crystallographically forbidden symmetries.

The discovery of quasicrystals (8) a dozen years ago was shocking because these solids exhibit 5-fold symmetry axes arranged in a three-dimensional icosahedral symmetry, the most famous forbidden crystal symmetry. The key property of quasicrystals is that their atomic structure is quasiperiodic, rather than periodic as in ordinary crystals (2–4). Instead of atoms repeating throughout the structure at some regular interval, as in ordinary (periodic) crystals, atoms in quasicrystals are spaced at long or short intervals that repeat with incommensurate frequencies. Incommensurate means that the frequency of long intervals divided by the frequency of short intervals is an irrational number, inexpressible as the ratio of integers. It is precisely because they are quasiperiodic that quasicrystals can violate the laws of periodic crystal symmetry developed by Bravais over 150 years ago. All previously forbidden symmetries are allowed for quasicrystals. These include 5-, 8-, and 12-fold symmetry axes, all of which have been observed in different materials since 1984. Some quasicrystals consist of periodically stacked layers in which atoms are packed quasiperiodically within each layer in one of the forbidden symmetry patterns. Others are quasiperiodic in all three dimensions and exhibit 5-fold axes arranged with icosahedral symmetry.

Just as periodic tilings are a powerful tool for visualizing the structure and properties of crystals, the Penrose tiling (1) has been influential in developing intuition about quasicrystals. Dov Levine, now at the Technion, and I had the Penrose tiling in mind when we first hypothesized the possibility of quasicrystals as a new phase of solid matter (2–4). The tiling is composed of two tiles, fat and skinny rhombi, that repeat with incommensurate frequency. As a result, the ratio of fat and skinny tiles is an irrational number, the golden mean so beloved by the Greeks. To force the tiles to make a quasiperiodic tiling, one must introduce matching rules for how any pair of tiles can join edge-to-edge. We showed that a three-dimensional analogue exists and proposed the possibility of quasicrystal solids in which each tile is replaced by a cluster of atoms. We further computed the diffraction pattern obtained by scattering electrons from quasicrystals with 5-fold symmetries axes and showed that it agreed with the pattern measured for the newly discovered icosahedral alloys.

In spite of the apparent success of the Penrose picture, concerns about the complex atomic interactions required to mimic the original Penrose matching rules have motivated alternative models for quasicrystals (9). Each treated quasicrystals as some kind of disordered phase that is thermodynamically metastable or stable only at high temperatures. In recent years, though, quasicrystals have been discovered whose diffraction properties, including dynamical scattering effects, indicate near-perfect quasiperiodic order (as perfect as the periodic order exhibited by the best metallic crystals) and whose structure apparently remains thermodynamically stable as temperature decreases (10). The newly discovered proper-

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ties of Penrose tilings buttress the theoretical case for the Penrose tiling picture by showing that the requirements can be reduced to those similar for crystals. The structure is reinterpreted in terms of a single repeating unit (e.g., an atomic cluster), just as for crystals, with the difference that neighboring clusters share atoms. Furthermore, this structural motif is suggested to play an integral role in energetics: quasicrystals form if sharing atoms is energetically favored (6).

Single Tile/Matching Rule

The first surprise is that a quasiperiodic tiling can be forced using a single type of tile combined with a matching rule (see Fig. 1). The tiling is unconventional (perhaps a better term is a "covering") since the decagon tiles are permitted to overlap, but only in certain discrete ways, *A* or *B* type. As an analogy to a real atomic structure, the overlaps should be construed as the sharing of atoms between neighboring clusters rather than interpenetration of two complete clusters. Realistic atomic models of known quasicrystals are known to incorporate clusters whose geometry enables sharing of atoms without distortion of the cluster shape (9, 11–14).

The decagon construction was originally proposed by P. Gummelt (7), who presented an elaborate proof. Jeong and I have found a very simple, alternative proof outlined below that makes clear the relation to Penrose tilings and leads us to a second novel scheme.

The proof is based on inscribing each decagon with a fat Penrose rhombus tile, as illustrated in Fig. 1c. The original Penrose tiling is constructed from fat and skinny rhombi with marked edges such that two edges may join only if the type and direction of arrows match (4, 15). Gummelt showed that, in a perfect decagon tiling, there are exactly nine ways a decagon can be surrounded by neighbors that have *A* or *B* overlaps with

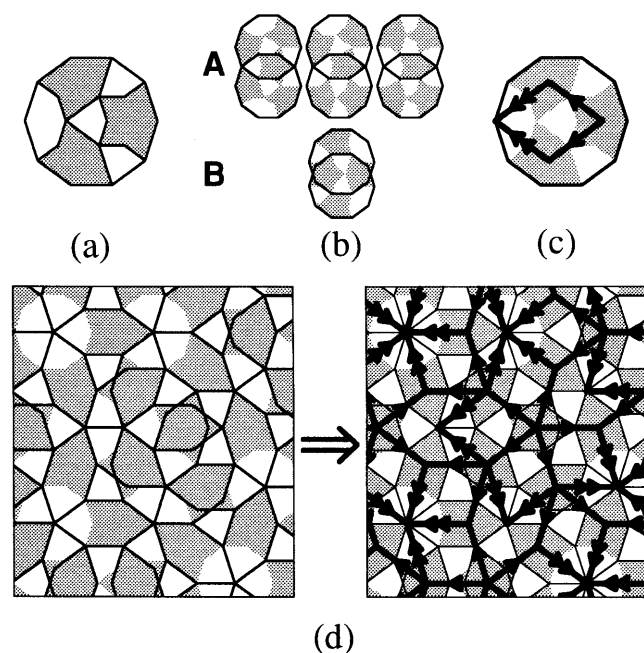


FIG. 1. Quasiperiodic tiling can be forced using a single tile, the marked decagons shown in *a*. Matching rules demand that two decagons may overlap, as shown in *b*, only if shaded regions overlap and the overlap area is greater than or equal to the hexagonal overlap region indicated as *A*. This permits two possible types of overlap between neighbors: either small (*A* type) or large (*B* type), as shown in *b*. If each decagon is inscribed with an fat rhombus, as shown in *c*, a tiling of overlapping decagons (*d* Left) can be transformed into a Penrose tiling (*d* Right), where space for the skinny rhombi incorporated.

it (7). The allowed configurations of overlapping decagons may be mapped into configurations of inscribed rhombi. For any two overlapping decagons, the inscribed rhombi share at least one vertex and sometimes share an edge. Where the rhombi join at a vertex only, there is an open angle formed by the edges that are the location and shape where skinny rhombi can be fit according to the Penrose matching rules. Seven of the nine decagon configurations correspond to completely surrounding an fat tile by neighboring tiles. In the other two cases, one rhombus vertex is incompletely surrounded; but, there are only two allowed ways of adding overlapping decagons so that the inscribed rhombi complete the vertex. Counting all of these, the decagon overlap rules map into eleven ways of completely surrounding a central fat tile with fat and skinny tiles, precisely the number and types allowed by the Penrose arrow rules. Restricting the surroundings of every fat tile to these eleven types is equivalent to enforcing the Penrose arrow rules for fat and skinny tiles; and, thus, the proof is completed. An important corollary is that the two-tile Penrose tiling can be reinterpreted in terms of a single repeating motif, suggesting a similar interpretation for quasicrystals.

Maximizing Cluster Density

The second surprise is that matching rules can be avoided. Instead, a perfect Penrose tiling can arise simply by maximizing the density of some chosen tile cluster, *C*. Imagine all possible tilings constructed from fat and skinny rhombi with no matching rules. These include quasiperiodic, periodic, and random tilings. Then, the claim is that the Penrose tiling uniquely has the maximum density of *C* clusters. (Two tilings are considered equivalent if they differ by patches whose density has zero measure.) The physical analogue is that *C* represents some low-energy microscopic cluster of atoms and that minimizing the energy naturally maximizes the cluster density and forces quasiperiodicity.

The cluster *C* is shown in Fig. 2. This choice is motivated by the fact that the *C* clusters in a Penrose tiling and the decagons in a decagon tiling are in one-to-one correspondence. Although they have different shapes, their key similarity is that two neighboring *C* clusters can share tiles in two ways isomorphic to the *A* and *B* overlaps of decagons. (The hexagon side wings in Fig. 2 are introduced to prevent other kinds of overlaps.) Hence, the Penrose tiling has the unique property that every *C* cluster has an *A* or *B* overlap with its neighbors. However, this does not prove that it has the maximum ρ_C , defined as the number of *C* clusters per unit area in units where an skinny rhombus has area equal to unity.

The proof uses the concept of "deflation." Deflation corresponds to replacing each complete *C* cluster by a larger,

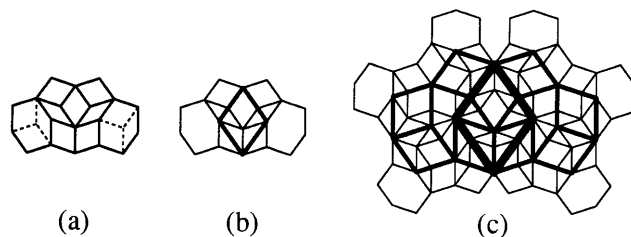


FIG. 2. Cluster *C* consists of five fat and two skinny rhombi with two side hexagons composed of two fat and one skinny rhombus each. There are two possible configurations for filling each side hexagon; the two possibilities are shown with dashed lines on either side in *a*. Under deflation, each *C* cluster can be replaced by a single "deflated" fat rhombus, as shown in *b*. There is a configuration of nine *C* clusters shown in *c* (thin lines) that, under deflation, forms a scaled-up *C* configuration (medium lines), called a *DC* cluster. Under double-deflation, each *DC* cluster is replaced by "doubly deflated" fat rhombus (thick lines).

“deflated” fat rhombus (see Fig. 2). The deflated rhombus has τ times the side length and times the area of the original, where $\tau = 1.618 \dots$ is the golden ratio. Because Penrose tilings are self-similar (1), the density of deflated fat rhombi equals τ^{-2} times the density of original fat rhombi, which equals the density of C clusters: $\rho_C^0 = 1/(3\tau + 1)$. The deflation operation can be repeated: identify all configurations of deflated rhombi that form a scaled-up version of the C cluster (call this configuration a DC cluster) and replace each with a yet-larger fat tile (see Fig. 2). Due to self-similarity, $\rho_{DC} = \rho_C^0/\tau^2$ for a Penrose tiling. For non-Penrose tilings, deflation corresponds to the same replacement wherever nine fat rhombi form a complete C cluster, but the deflated tiling is not necessarily similar to the original and may include voids. Our proof is by contradiction: If a tiling existed with $\rho_C > 1/(3\tau + 1)$, then deflating it repeatedly increases the density without bound—an impossibility.

Because the C clusters can overlap, a reliable scheme for assigning, or at least bounding, the area occupied by a given C cluster is needed. A useful trick is to decorate each C cluster as shown in Fig. 3. The kite-shaped region, which has area $3\tau + 2$, will be called the “core area” of the C cluster. Although C clusters can overlap to some degree, the only possibilities for close overlap are A overlaps, in which the core areas meet along an edge; or B overlaps, in which there is a specific overlap of core areas (Fig. 3). In a Penrose tiling, these core areas fill the entire plane without holes. If the core area of a C cluster is not overlapped by any neighboring core areas, it can be assigned the entire core area (at least that); for these cases, the C clusters occupy area greater than or equal to $3\tau + 2$, so they decrease the density relative to the Penrose value $\rho_C = 1/(3\tau + 1)$. Two C clusters with B overlaps are assigned area less than $3\tau + 1$ due to the overlapped core areas. Hence, an important conclusion is reached: B overlaps are the only mechanism for exceeding Penrose density.

To exceed the Penrose density, a tiling must have a greater density of B overlaps than Penrose tiling. However, this condition is not sufficient. In Penrose tiling, every B overlap of two C clusters is surrounded by a DC cluster (see Figs. 2 and 3). In a non-Penrose tiling, a fraction of B overlaps may not be part of a DC cluster (i.e., one or more of the seven other C clusters that compose a DC cluster is not present). In these cases, it is straightforward to show by explicit constructions that one can always identify an area attached to the associated B overlap that does not belong to the core area of any C cluster and is not associated with any other B overlap. This “extra” unassigned area occupies at least as much area as saved by the B overlap. Hence, a B overlap that is not part of a DC cluster does not contribute to increasing the density of C clusters above the Penrose value.

Suppose there were a tiling with a density of C clusters greater than the Penrose value. Then, it has just been shown that it must have a higher density of DC clusters than in a Penrose tiling, $R_{DC} > \tau^{-2}$, where R_{DC} is the number of DC

clusters divided by the number of C clusters. Under deflation and rescaling the area by τ^{-2} , each DC cluster becomes a C cluster of the deflated tiling whose density is $\tau^2 R_{DC} \rho_C$. Since R_{DC} is more than τ^{-2} , the deflated tiling has a density of C clusters that is strictly greater than the original tiling. Repeating the deflation ad infinitum would lead to an impossible tiling with an unbounded density of C clusters. A corollary is that, if the C cluster density equals the Penrose value, then $R_{DC} = \tau^{-2}$ (the Penrose tiling value) and the C cluster density in the deflated tiling must equal the Penrose value. This is useful in proving that the Penrose tiling is the unique tiling with $\rho_C = 1/(3\tau + 1)$. Suppose there were a non-Penrose tiling with the same density. It has been argued that the only local configurations that can increase the density above the Penrose value are DC clusters and that the increase in density is due to the B overlap of core areas, which is the same for each DC cluster. The corollary says that the hypothetical tiling has the same density of DC clusters and, hence, the same density of B overlaps surrounded by DC clusters as Penrose tiling. However, by definition, the non-Penrose tiling must also have patches with nonzero area measure, which violate the Penrose matching rules and so cannot belong to the core area of any C cluster. Since the DC cluster density is the same but there are these patches, it would appear that the average area per C cluster must be less than the Penrose density. The only conceivable exception would be if there happen to be additional B overlaps that do not belong to DC clusters whose overlap area exactly compensates the area of the patches. Even this possibility can be eliminated because the corollary states that $R_{DC} = \tau^{-2}$, which means that the density of C clusters remains unchanged under deflation and rescaling. Yet, the patches grow: a patch excluded from a C cluster must also be excluded from a DC cluster, but also, some C clusters that border the patches cannot be part of a DC cluster and add to the patch area. Since the number of C clusters remains fixed but the patches grow, the C cluster density in the deflated tiling must be less than the Penrose value. This contradicts the corollary; hence, uniqueness is established.

Implications

The two new approaches to Penrose tiling, a single tile type and maximizing cluster density, can be combined. Together, they suggest a new view of the structure of quasicrystals and why they form.

The atomic structure can be reinterpreted in terms of a single repeating cluster, rather than two different clusters. This simplifies atomic modeling since atomic decoration of only the single cluster need be considered. The modeling is further constrained since the cluster must be capable of sharing atoms in certain discrete ways with neighbors.

The results also suggest physically plausible conditions that can lead to quasicrystal formation, shedding new light on an old mystery. They imply that quasicrystals can be understood by considering the energetics of microscopic clusters and that cluster overlap is an important structural element, establishing an earlier conjecture (6).

The simplest energetics would be assigning negative energy to the clusters and zero energy to all other local configurations, since this is sufficient to cause the minimum free energy state to be the maximum cluster density state. However, it is important that the energetics be robust. Some experiments with other energetics assignments suggest that there is a continuum of possibilities that lead to the same Penrose ground state, but this needs to be studied further.

All of these concepts can be tested using the atom clusters of known quasicrystals. Our two-dimensional tiling results can most readily be applied to decagonal quasicrystals that have periodically spaced layers with Penrose tiling structure. The extension to three-dimensional icosahedral symmetry is a

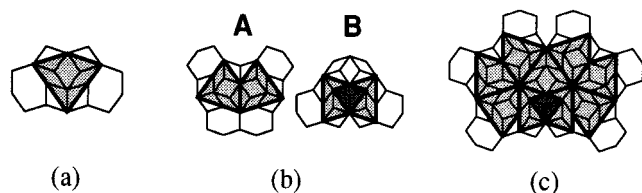


FIG. 3. Associated with each C cluster is core area (with area $3\tau + 2$) consisting of a kite-shaped region, shown as shaded in *a*. In a Penrose tiling, core areas of neighboring tiles either join edge-to-edge (A overlap) or overlap by a fixed amount (B overlap), as shown with dark shading in *b*. *c* is a DC cluster that illustrates the core areas of the nine C clusters that compose it. An isolated DC cluster contains one B overlap (see dark shading) and the rest A overlaps.

future challenge, although past experience suggests that two-dimensional properties can be extended to three-dimensions. If these principles can be established, they may enable the reliable prediction of new quasicrystals.

As an example of the application of symmetry principles, the subject of quasicrystals is still in a primitive stage. The Bravais classification of crystal point symmetries, as well as space groups, has been achieved. But, the key confusions about the structure and formation of quasicrystals, as described in this paper, go beyond symmetry classification. Herein, our concept of quasicrystals has been heavily influenced by experience with Penrose tilings and Penrose matching rules. Based on the original rules, it appeared that two or more repeating units, rigid matching rules and nonlocal growth rules were required to build the structure. All of these have been shown to be unnecessary, but only by further imaginative tiling constructions. Even so, it is uncertain, without more constructions, whether the results generalize to other symmetries and other dimensions. What is missing are powerful mathematical techniques analogous to the group theoretic methods applied to the structure periodic crystals 150 years ago. Our ultimate challenge is to understand how the new results shown in this paper arise directly from quasiperiodicity and crystallographically forbidden symmetries.

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